

THE MYTH OF PYROPHORIC CARBON

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The Myth of Pyrophoric Carbon

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ABSTRACT

The hypothesis of "pyrophoric carbon," that cooking causes chemical enhancement of self-heating properties, is inconsistent with measurements of the self-heating parameters of cooked and uncooked wood chips. These tests employed a recently-introduced experimental method that offers advantages over traditional iterative techniques. Predicted critical sizes and temperatures are higher for the cooked material than the uncooked. The additional effects of cooking-induced reductions in the thermal inertia, due mainly to lowered density, are quantified experimentally. The cause of delayed ignition of whole wood is shown to be diffusion-controlled self-heating facilitated by cooking. The delay is caused by long-term effects of cooking on the physical structure of wood cells, which consist of long, slender tubes. This microstructure, when undamaged, accounts for high axial permeability but low transverse permeability, with ratios on the order of $10^4:1$ for the softwoods typically used as structural lumber. Cooking eventually allows oxygen access deep into whole wood via greatly enhanced transverse permeability caused by disruption to the microstructure in the form of transverse cracks. Lack of oxygen diffusion prior to cooking prevents self-heating in whole wood except near end-grain surfaces. These processes are demonstrated experimentally.

KEYWORDS: Pyrophoric carbon, pyrophoric char, wood ignition, self heating, thermal explosion, spontaneous ignition, thermal inertia, wood permeability

Nomenclature

A	Frequency factor	Q	Heat of reaction
Bi	Biot number, hr/k	r	Characteristic dimension
c	Specific heat capacity	R	Universal gas constant
E	Activation energy	t	Time
f	Fraction of air-dry weight remaining	T	Temperature
h	Heat transfer coefficient	x	Spatial coordinate
I	Ratio of thermal inertias	α	Thermal diffusivity, $k/\rho c$
k	Thermal conductivity	δ	Frank-Kamenetskii parameter
M	Intercept on iterative-method plot	ϵ	E/RT
N	Intercept on transient-method plot	ρ	Mass density
P	E/R , slope	θ	Dimensionless temperature
q	Heat release rate		

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I. INTRODUCTION

In the practice of forensic fire investigation, the concept of "pyrophoric carbon" holds that when wood is held at elevated but sub-ignition temperatures for long periods, a chemical process lowers the "ignition temperature" of the material.^{1,2,3,4,5,6,7,8,9} Ultimately, it is hypothesized, the "ignition temperature" is lowered to the exposure temperature and a fire commences. The first fires attributed to this process involved steam pipes in the 19th century. A search was conducted of the US government National Fire Incident Reporting System for incidents involving non-flame heat sources igniting sawn wood—criteria fitting the "pyrophoric carbon" attribution. It reveals annual averages from 1985 to 1996 of 8000 incidents, \$100 million US in damage, 50 deaths, and 600 injuries.

A comprehensive literature review¹⁰ has shown that the term, "pyrophoric carbon," was introduced in 1872¹¹ as an hypothesis for the cause of haystack fires. The word "pyrophoria" is the English translation of *pyrophorie*,¹² meaning the capability of self-heating. This hypothesis made its way into the fire-investigation literature around the turn of the century.¹³ Since then, it has been repeated with regularity, but has only occasionally been subjected to limited scientific scrutiny.^{14,15,16,17,18,19,20} This review of literature spanning 125 years failed to reveal any controlled laboratory data supporting the "pyrophoric carbon" hypothesis.¹⁰ The phenomena of interest are field reports of ignition apparently arising from the exposure of cellulosic materials—usually whole wood—to heat sources over extended periods. Post-fire investigation generally fails to demonstrate that ignition is possible under the suspected circumstances, since the purported exposure temperatures are lower than what had been recognized as possible for ignition. These field-reported phenomena are referred to here as "delayed ignition."

This paper reports a variety of experiments that examine the hypothesis of "pyrophoric carbon," and an alternative hypothesis that physical—not chemical—processes are responsible for delayed ignition. In the first section, the analytic and experimental methods of self-heating are reviewed, including a recently-introduced laboratory technique. The results of self-heating tests on cooked and uncooked wood chips are presented that show that cooking does not cause chemical enhancement of wood's self-heating properties. Next, the effect of cooking on the thermal inertia of wood is determined experimentally. Finally, two demonstration tests on whole-wood self heating are presented. The longitudinal permeability of whole wood is shown to support self heating, while the low transverse permeability inhibits self heating by severely restricting the transport of oxygen. These tests demonstrate that the physical damage, in the form of fissure generation caused by prolonged cooking, eventually eliminates the oxygen deficiency, culminating in self heating to ignition. Once the oxygen inhibition is removed, the field-reported, long-delayed ignitions are caused by the classic "hot spot" type of self heating.

II. EXPERIMENTAL METHODS

Since this study focuses on the lower bound on "ignition temperature," the pertinent mechanism is self heating to solid-phase ignition, and not the higher-temperature types of ignition such as piloted- or auto-ignition of gaseous pyrolyzate. The most common self-heating model is that of Frank-Kamenetskii. He showed that self heating to ignition can be predicted based on the existence of solutions to the system's steady-state energy equation.²² The general energy equation for a self-heating solid is

$$\rho c \frac{\partial T}{\partial t} = k \nabla^2 T + q(T), \quad (1)$$

where the variables are listed in the nomenclature. It is assumed that 1. The material is homogenous, isotropic, and has properties independent of temperature and time. 2. The material is sufficiently porous that the supply of reactants is unlimited. 3. The transport mechanism within the body is only diffusion. 4. Heat generation is governed by a single

Arrhenius reaction, $q(T) = \rho Q A \exp(-E/RT)$ where the pre-exponential term is the maximum heat release rate per unit volume. 5. The normalized activation energy is high compared to the surrounding temperature. That is, $\epsilon_A = RT_A/E \ll 1$ where the subscript, A , indicates ambient. For the existence of critical behavior, ϵ_A is strictly limited to less than 0.25.²³ This condition is easily met for this study since values of E/R are on the order of 10^4 K.

Nondimensionalizing the spatial coordinate on the system's maximum size, r , the general, dimensionless, steady-state energy equation is

$$\nabla^2 \theta + \delta \exp(\theta) = 0, \quad (2)$$

where θ is the dimensionless temperature given by

$$\theta \equiv \frac{E}{R} \frac{T - T_A}{T_A^2}, \quad (3)$$

and δ is the Frank-Kamenetskii parameter,

$$\delta \equiv \frac{1}{\alpha} \frac{Q A}{c_p} \frac{E}{R} \frac{r^2}{T_A^2} \exp\left(-\frac{E}{R} \frac{1}{T_A}\right) = \frac{\rho Q A E}{k R} \frac{r^2}{T_A^2} \exp\left(-\frac{E}{R T_A}\right). \quad (4)$$

For a given geometry, Eqn. (2) is subject to the boundary conditions

$$\nabla \theta|_0 = 0 \quad \text{and} \quad \theta|_1 = 0, \quad (5)$$

where an infinite average surface Biot number is assumed and δ is a parameter. There is a maximum value of δ for which a solution to Eqn. (2) exists, δ_c , which is known as the critical Frank-Kamenetski parameter. δ_c is primarily a function of geometric shape of the solid and the average surface Biot number. Correction coefficients can account for violations of the assumptions list above. Beever²⁴ gives an excellent review of critical parameters for various geometries and the corrections required for proper application.

In the experimental implementation of the Frank-Kamenetskii model, Eqn. (4) is rearranged as

$$\ln \frac{\delta_c T_A^2}{r^2} = \ln \frac{E}{\alpha R} \frac{Q A}{c} - \frac{E/R}{T_A} = M - \frac{P}{T_A}. \quad (6)$$

Plotting this equation as $\ln \frac{\delta_c T_A^2}{r^2}$ versus $1/T_A$ allows the activation energy to be determined

from the slope, P , and the pre-exponential from the intercept M . Stability tests are conducted in convection ovens on varying sizes of samples, usually cubes, to determine the critical temperature, T_c , for each size. Each experiment consists of placing the prepared sample into a preheated isothermal oven. If the center temperature exhibits thermal runaway, the critical ambient (oven) temperature for that size is lower, and a lower oven temperature is selected until the critical temperature is bracketed with sufficient accuracy. Ultimately, knowing δ_c , P , and M , Eqn. (6) can be used to predict critical temperatures as a function of size for the material under study. In practice, this method can become cumbersome because of the lengthy experimental iteration process to determine M and P . In addition, large amounts of material are required, the Biot number must be estimated, and, as the critical condition is approached, the times to thermal runaway become lengthy.

Chen and Chong^{25,26} introduced a novel approach, which is used here, for evaluation of the chemical kinetic parameters governing self-heating behavior. Consider the transient energy equation for a slab of half-width r ,

$$c \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \rho Q A \exp\left(-\frac{E}{R T}\right). \quad (7)$$

The initial condition is assumed to be $T=T_0$ at $t=0$ and the boundary conditions are

$$k \frac{dT}{dx} = 0 \quad \text{at } x=0,$$

and

$$-k \frac{dT}{dx} = h(T_s - T_A) \quad \text{at } x=r.$$

This is the slab dunking problem with heat generation. It describes the transient temperature distribution in a reactive specimen, after it is placed in an oven at T_A .

The assumptions include 1-4 listed above in the Frank-Kamenetskii model with one addition: at some instant in its transient heating the temperature profile in a central region of the sample becomes uniform, with negligible gradients.

Fig. 1 illustrates the progression of self-heating in a slab. Early in the event, the peak temperatures are at the surface as the specimen is heated by the oven. As self-heating begins

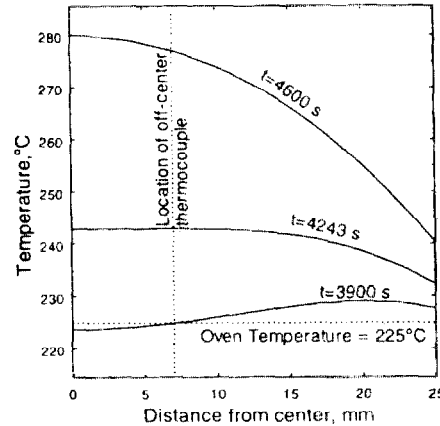


Figure 1 An illustration of the transient method. These are the results of a numerical model of a self-heating slab. The parameters are: $h=22 \text{ W/m}^2\text{K}$, $k=0.1 \text{ W/mK}$, $\alpha=2 \times 10^{-7} \text{ m}^2/\text{s}$, half-width=25 mm, $QA/c=583 \text{ K/s}$, $E/R=8300 \text{ K}$. The three plots are examples of temperature profiles at key phases of self heating. The lower plot shows the characteristic S curve that occurs early, as conduction of oven heat combines with self heating near the surface. The middle plot shows the crossing point condition where the profile near the center of the slab is nearly flat. The upper plot shows the final phase where self heating has become fully established, with the peak temperature at the center.

the maxima move inward. As the dual maxima join to form a single central maximum, there is an instant at which the central temperature profile is nearly flat. That is, the first two distance derivatives are near zero, so the conduction term vanishes. $\partial^2 T / \partial x^2$ at the center-plane is initially zero, climbs to a maximum positive value during heat up, then declines and finally

goes negative as thermal runaway occurs. At the unique time when $\left. \frac{\partial^2 T}{\partial x^2} \right|_{x=0}$ crosses zero, Eqn. (7) at the center plane, $x=0$, becomes

$$\left. \frac{\partial T}{\partial t} \right|_{x=0} = \frac{QA}{c} \exp\left(-\frac{E}{RT_p}\right), \quad (10)$$

where T_p is the center-plane temperature at which the conduction term vanishes. At this point the central region of the sample is adiabatic—the surrounding material momentarily taking the role of guard heater.

Since Eqn. (10) can be written as

$$\ln \left. \frac{\partial T}{\partial t} \right|_{x=0} = \ln \frac{QA}{c} - \frac{E}{RT_p}, \quad (11)$$

a plot of $\ln \left. \frac{\partial T}{\partial t} \right|_{x=0}$ versus $1/T_p$ yields a straight line whose slope, $-E/R$, gives the activation energy and whose intercept gives the pre-exponential as $\ln QA/c$, the log of the theoretical

maximum adiabatic rate of temperature rise. The comparison between the intercepts of Eqns. (6 and 11) is clarified if Eqn. (11) is written as

$$\ln \frac{\partial T}{\partial t} = N - \frac{P}{T_p}, \quad (12)$$

where $N = \ln \frac{QA}{c}$, and P is the same as in Eqn. (6), then

$$N = M - \ln \frac{P}{\alpha}. \quad (13)$$

Notice that since it is the central adiabatic material whose properties are measured, the accuracy of the experimentally measured T_p and $\left. \frac{\partial T}{\partial t} \right|_{x=0}$ are unaffected by the boundary conditions at the adiabatic moment. Thus, no correction is needed in the interpretation of the measured values to account for oven heat transfer rates. Of course, the boundary conditions control the values of T_p and $\left. \frac{\partial T}{\partial t} \right|_{x=0}$ that are obtained on each test. Indeed, experimentally, variations in T_p are produced by varying the oven air temperature or by varying the size of the sample. While retaining the goal of evaluating the self-heating kinetic parameters, the transient test method offers advantages over the standard method. First, almost every test results in a data point on the graph, even if the oven temperature is sub-critical. Further, it eliminates the direct Biot number effects on data interpretation. Moreover, δ_c need not be evaluated in the experiments. This means that the heat transfer coefficient in the oven and the conductivity of the sample need not be known during the experiments. The transient method allows for reuse of previously tested samples because the test can be halted before substantial reactant consumption occurs. Finally, the plot (see e.g. Fig. 4) produced by Eqn. (11), $\ln \left. \frac{\partial T}{\partial t} \right|_{x=0}$ versus $1/T_p$, can be viewed as a reaction-rate versus temperature plot, and as such may provide useful insight into the self-heating character of the material.

III. EFFECT OF COOKING ON WOOD CHEMISTRY

In order to eliminate the dominating effects of the physical microstructure of wood, the samples used in these experiments were chipped into thin, irregular slabs, approximately 1 mm in thinnest dimension. A portion of the Douglas fir chips were cooked down to 42% of the dry, uncooked weight which is near the asymptotic value for remaining weight.²⁷ The chip depth in a set of stainless steel trays was limited to 20 mm to avoid self heating during cooking at 200°C in an oven with vigorous air circulation for about ten days. Photo 1 shows the uncooked and cooked chips. The test samples were loaded into 50 and 100 mm cubic baskets made of stainless-steel wire mesh with 0.25 mm wires spaced 1.6 mm apart. Two 0.5 mm, bare-wire type-K thermocouples were inserted at the center and at 25% of the cube half-width from the center on one principal axis. A null difference between the two probes was taken as the indication of a flat temperature profile. Fig. 2 shows the temperature histories for a typical test run. A detailed error analysis based on numerical modeling of a slab showed that the worst-case error is small—less than 6% of N and P in Eqn. (12).¹⁰ Thermocouple positioning errors tend to have little effect on the chemical kinetic parameters because T_p and dT/dt are simultaneously biased in a way that moves the data point in a direction parallel to the linear fit line.¹⁰

Fig. 3 shows the self-heating data for cooked and uncooked Douglas fir. The uncooked wood results are extremely linear, with a correlation coefficient of 0.998. The uncooked activation energy is 8250 K, which is compared in Table 1 to the self-heating

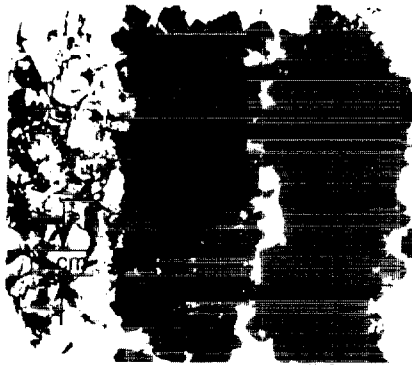


Photo 1 Uncooked, cooked, and charred wood chips.

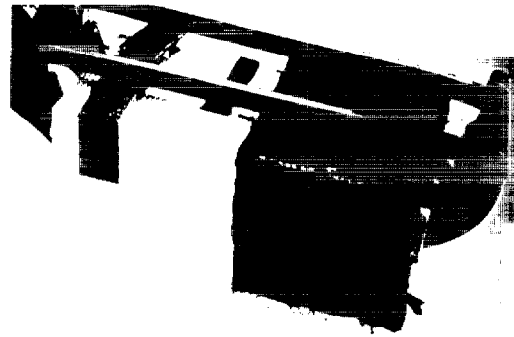


Photo 2 Twin-Rayleigh experimental arrangement. The reference specimen, an 89 mm cube, is uncooked Douglas fir. The specimen on the right is the same material—cut from an adjacent portion of timber—after more than 10 days of cooking at 200 C. The interface thermocouple is centered on the contact face. Not shown are the thermocouples that penetrate to the geometric center of each block, entering through and normal to the faces opposite the interfacial plane. The end-grain faces of the cooked block are sealed.

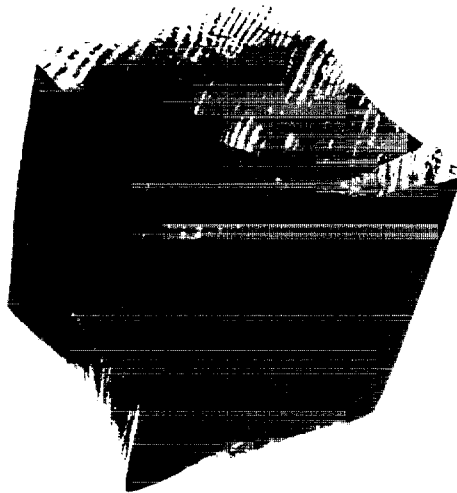


Photo 3 An 89 mm cube after self-heating at 200 C. Solid-phase ignition occurred on the end-grain faces, while the side-grain faces exhibited little damage. Note the greater shrinkage at the end-grain faces than at the center. Unlike isotropically porous materials which the highest self-heating temperatures are at the center, the highest temperatures in self heating whole wood are near the end-grain faces.

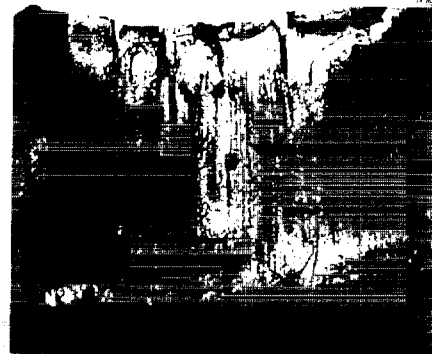


Photo 4 A self-heated 89 mm cube split open along a nearly-diagonal growth ring. The hourglass heat pattern indicates that the regions of maximum oxidation reaction are near the end-grain faces and along the axial centerline.

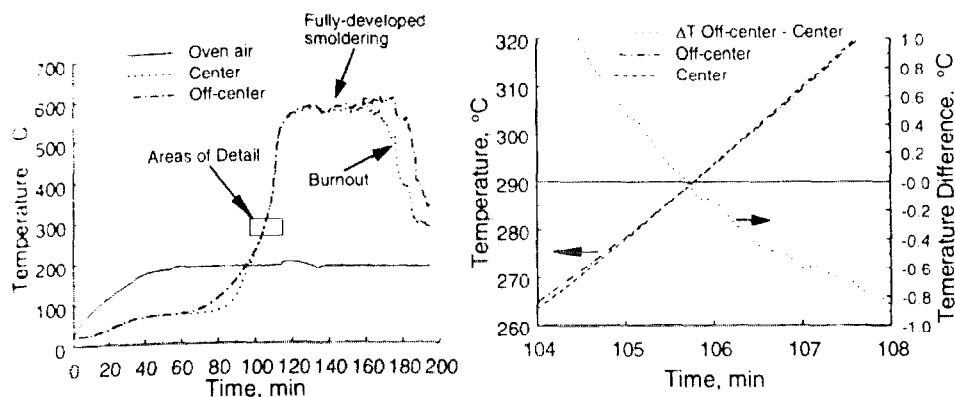


Figure 2. A typical test history with all data shown at left, and detail of crossing point shown at right. This sample exhibited thermal runaway, ignition, and burnout. These data are for a 100 mm cube of uncooked wood chips. $T_p = 288.2^\circ\text{C}$, $dT/dt|_{x=0} = 15.7 \text{ K/min}$.

parameters reported in the literature from other experiments on wood chips and sawdust.^{23,28} The effect of cooking is manifold. First, it lowers the heat release rate over most of the tested temperature range. At the highest tested temperatures—above 274°C , or 76°C higher than the cooking temperature—a small increase appears. In the middle temperatures there is an aging effect. When initially tested there was a relatively low heat release rate, but with 10 days ageing it became even lower. Fig. 4 is a stability chart based on these data showing the sizes and ambient temperatures of cubes that will and will not self-heat to ignition. These data show that the actual effect of cooking is contrary to the “pyrophoric carbon” hypothesis. The chemical kinetic parameters of cooked wood make it more difficult to self heat to ignition than uncooked wood over the temperature range of interest to the delayed ignition problem. Therefore, “pyrophoric carbon” appears not to exist.

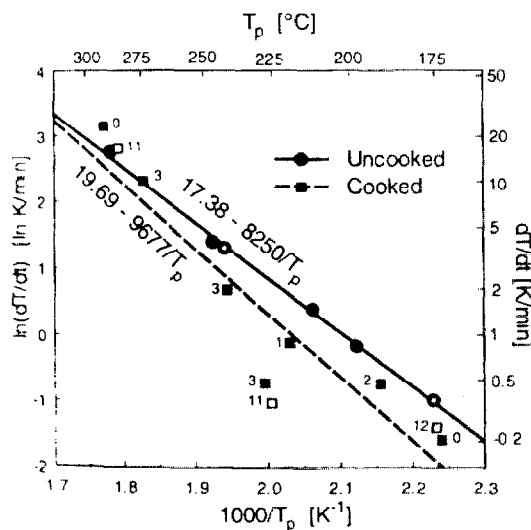


Figure 3 Comparison of the self-heating properties of cooked and uncooked wood chips. The numbers by the cooked data points are the days between removal from the 200°C cooking oven and the self-heating test. Hollow squares are tests at lower sample density—75% of the density of the solid squares. Hollow circles indicate that the specimen was reused after a previous test. The region of practical import to wood self heating is $\leq 250^\circ\text{C}$.

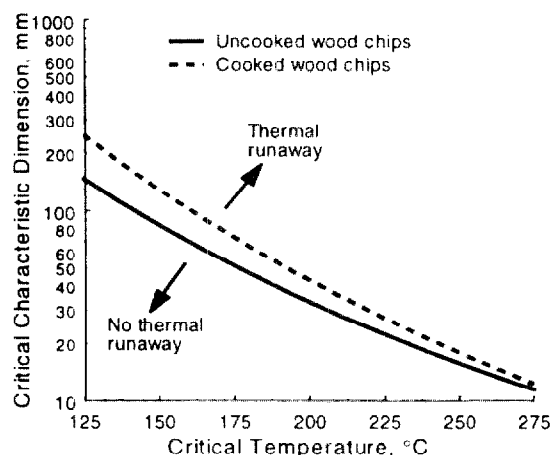


Figure 4 Stability map showing the effect of cooking on critical values for Douglas fir chips. Below the critical size and temperature, thermal runaway will not occur; above, runaway followed by ignition will occur. The cooked wood remains stable—it does not exhibit thermal runaway—with larger sizes and at higher temperatures than uncooked wood chips. The assumed Frank-Kamenetskii parameter is 2.52, the exact value for a cube with no corrections.

MATERIAL	P [K] = E/R	M [K ² /mm ²] = $\ln \frac{E}{\alpha R} \frac{QA}{c}$	N [K/min] = $\ln \frac{QA}{c}$	Critical characteristic dimension at $\delta_c = 2.52$, [mm]		
				150°C	200°C	250°C
Wood sawdust ²⁹	13030	34.95	28.18	84.0	18.5	5.5
Uncooked Monterey pine ²⁶	10850	29.66	23.08	90.1	26.0	9.6
Uncooked Douglas fir chips	8251	23.69	17.38	82.6	33.0	15.8
Cooked Douglas fir chips	9677	26.16	19.69	129.7	43.3	18.0

Table 1 A tabulation of self-heating parameters with critical sizes at selected temperatures. The fuels in the bottom three rows were evaluated with the transient method. The sawdust in the top row was evaluated with the iterative method. The conversions between M and N assume a thermal diffusivity of 2.5×10^{-7} m²/sec.

IV. EFFECT OF COOKING ON THERMAL INERTIA

The effect of thermal inertia, $k\rho c$, on flaming ignition is significant because of its influence on the ease with which incident heat flux raises the surface temperature.³⁰ There is little in the literature on the effect of cooking on thermal inertia in wood, and the effect of reduced thermal inertia on self-heating behavior. It is known that cooking causes a reduction in density,³¹ and that conductivity correlates strongly with density and moisture content.³³ In this section a direct, self-referential method of measurement of thermal inertia is presented. The influence of thermal inertia on self-heating to ignition is discussed.

To track the effect of cooking on thermal inertia, the "twin-Rayleigh" method is used. This refers to the heat transfer problem of two semi-infinite solids with different uniform initial temperatures that are brought into contact at time zero, as shown in Photo 2. One block is a reference block kept at room temperature, and the other is an originally-identical twin cut from the same whole-wood specimen. The second block is held in an oven at a specified cooking temperature and removed only for periodic testing against its uncooked reference twin. The wood grain pattern of the two specimens is oriented to produce, as closely as possible, mirror symmetry about the interfacial plane.

From the Rayleigh problem solution,³² the ratio of the two thermal inertias is:

$$I \equiv \left(\frac{T_u - T_s}{T_s - T_c} \right)^2 = \frac{(k\rho c)_c}{(k\rho c)_u} \quad (14)$$

Since I is based on only three measured temperatures, it can be directly obtained by pressing together hot and cold cubes.

Figure 5 shows the results of such a test for 89 mm cubes, with a 200°C cooking temperature which are consistent with literature³³ changes in k , ρ , and c . The interfacial temperature was measured with a 0.05 mm thick ribbon thermocouple, and the two initial temperatures were measured with thermocouple junctions placed at their centers. The lowest I value measured before the cooked specimen became structurally unsound was 0.36 at $f=0.53$. This is an intrinsic limitation in the method, since it depends on a clamping load to produce direct contact between the two solids.

The effect of changes in heat transfer properties by cooking on the critical self-heating parameters is small because as thermal conductivity declines so does density, and these two effects largely cancel as seen in the expression for the Frank-Kamenetskii parameter, Eqn. (4). A lower thermal conductivity causes enhanced heat retention in the solid, but concomitantly the lower mass density lowers the chemical heat release per unit volume at a given temperature. The only remaining effect is through the Biot number corrections to δ_c , which are relatively small and make self heating less likely as I decreases. As the Biot number increases with lower solid thermal conductivity, the critical ignition temperature in a given problem increases.²⁴ Decreasing thermal inertia does, however, decrease the induction period, with greater effect as the temperature above critical increases. This could be significant in practical situations where wood is exposed periodically to high temperatures of short duration.

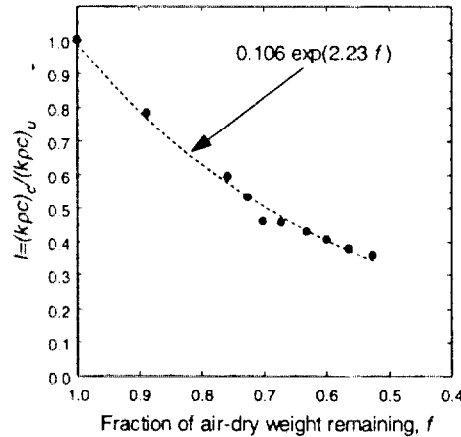


Figure 5 The effect of wood cooking on thermal inertia. Air-dry means in equilibrium with ambient conditions. Measurements are made at the time of initial pressed contact between the specimens, which are 89 mm cubes of Douglas fir.

V. WHOLE-WOOD DEMONSTRATION EXPERIMENTS

To study the effects of wood microstructure on whole-wood self heating, a number of exploratory oven tests were performed; this section reports the two most significant results.¹⁰ The geometric nomenclature of whole wood is depicted in Fig. 6.

Photo 3 is a 90 mm Douglas fir cube that had self-heated and ignited on the end grain in a 200°C oven. It was removed and extinguished before the smoldering caused excessive damage. There was a pronounced increase in transverse shrinkage going from the center of the block to the end-grain faces, indicative of greater heat generation near the end-grain faces. Indeed, breaking open the cube along a nearly-diagonal growth ring, shown in Photo 4, reveals a striking heat-affected pattern in the shape of an hourglass with the bell mouths at the end-grain faces. The narrow neck of the hourglass is midway between the two end-grain faces. This is in contrast to the centered sphere seen in isotropic materials and in accordance with the

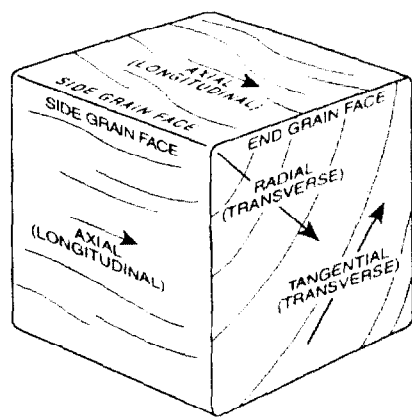


Figure 6 Nomenclature of whole-wood geometry.

should reduce the tendency to self heat because it hastens the escape of heat. Thus, anisotropic conductivity is not the explanation.

Permeability, on the other hand, is a major anisotropic property in wood. The ratio of axial to transverse permeability for softwoods is approximately 20,000.³⁵ This factor seems

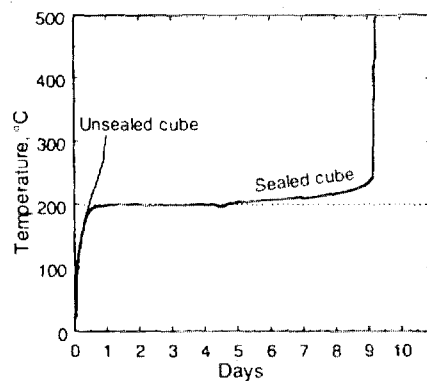


Figure 7 Center thermocouple measurements for two self-heating 200 mm whole-wood cubes with and without sealed end-grain faces. In both cases, the oven temperature is 200°C. The unsealed cube self heats to thermal runaway with only a one-day heat transfer delay. In contrast, the cube with sealed end-grain faces requires nine days before thermal runaway occurs, at which time sufficient fissures and cracks had developed to allow oxygen access to the interior.

principles of self-heating discussed earlier. The end-grain faces appear to promote self-heating, and the side grain faces appear to inhibit self-heating.

These experiments showed that some anisotropic property in whole wood profoundly affects its self-heating behavior. But which property? The thermal conductivity with the grain is typically 1.8 times the cross-grain conductivity.³³ Vyas and Welker³⁴ observed that for high heating rates causing flaming ignition, this higher axial conductivity delays ignition by increasing thermal inertia in tests where the end grain is exposed to the heat source. Side-grain faces ignited faster than end-grain faces when exposed to the same flux. But in the present tests at lower temperatures and lower heat fluxes that emphasize self-heating effects, the end-grain faces ignited while the side-grain faces did not. Moreover, according to self-heating theory, higher conductivity

should reduce the tendency to self heat because it hastens the escape of heat. Thus, anisotropic conductivity is not the explanation. Permeability, on the other hand, is a major anisotropic property in wood. The ratio of axial to transverse permeability for softwoods is approximately 20,000.³⁵ This factor seems consistent with the hourglass heat pattern, which could be caused by the combination of oxygen depletion far from the end-grain face and heat loss close to the side-grain faces. The next step then, was to test this hypothesis by counteracting the anisotropy by sealing the end grain of the specimen. This may also simulate a long timber that is exposed to a heat source midway along its length.

On a 200 mm Douglas fir cube the end-grain was sealed with commercially available RTV sealer.³⁶ This 200 mm cubic specimen was placed in a 200°C oven—well above the predicted critical temperature of about 120°C based on the wood chip experiments described in a previous section. Fig. 7 shows the temperature history for the nine days, along with a comparison plot of an identical unsealed cube under similar conditions. The unsealed cube ignited in one day. After five days, the sealed specimen began to exhibit surface fissuring and sub-runaway self-heating commenced. At nine days, with pronounced fissuring, it exhibited thermal runaway.

These experiments demonstrate that delayed ignition can occur by producing it under controlled laboratory conditions. Self heating in whole wood is a diffusion-controlled process. Long-term heating may cause important changes

in transverse permeability, important enough to allow self-heating to ignition. In practical applications, the proximity of the end grain, and hence of more easily diffused oxygen, to the heat source may play a role in the occurrence or avoidance of thermal runaway.

VI. CONCLUSIONS

This study has examined the hypothesis of "pyrophoric carbon," which some fire investigators have invoked to explain delayed ignition of solid wood. Typical accidental fires of this type are marked by cooking of whole-wood structural members for periods ranging from days to as long as years, culminating in solid-phase (smoldering) ignition. Cooking occurs when wood is subjected to temperatures high enough to cause physical and chemical alterations, but too low to cause ignition. It has been shown here that the chemical alterations caused by cooking do not enhance the self-heating properties of wood. In contrast, physical changes caused by cooking do facilitate self heating of whole wood by creating substantial transverse permeability which enhances oxygen diffusion into the interior. The delayed ignition of whole wood is due to physical alterations, not "pyrophoric carbon."

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VII. REFERENCES

1. Moore, W.W., "Spontaneous Combustion," *Quarterly of the National Fire Protection Association*, **6:2**, 188-198, 1912.
2. Underwriters' Laboratories, Inc., "Wood, Ignition of at Low Temperatures," *Data Card C60*, Serial No. UL198, Chicago, IL, January 1940.
3. McNaughton, G.C., "Ignition and Charring Temperatures of Wood," *Wood Products*, **50**, 21-22, 1945.
4. Carroll, J.R., *Physical and Technical Aspects of Fire and Arson Investigation*, pp 67, 330, Thomas, Springfield, IL, 1979.
5. DeHaan, J.D., *Kirk's Fire Investigation*, 2nd ed., , pp 48, 130, John Wiley, New York, 1983.
6. O'Connor, J. J., *Practical Fire and Arson Investigation*, p. 64, Elsevier, New York, 1987.
7. Bassano, J.R., "Pyrophoric Carbon," *With New York Firemen* **4**, 22, 1988.
8. Hobson, C.B., *Fire Investigation: A New Concept*, p. 17, Thomas, Springfield, IL, 1991.
9. DeHaan, J.D., *Kirk's Fire Investigation*. 3rd ed., pp 55, 140, John Wiley, New York, 1991.
10. Cuzzillo, B.R., *Pyrophoria*, Doctoral Dissertation, Department of Mechanical Engineering, University of California at Berkeley, Berkeley, CA, December 1997.
11. Ranke, H. von, "Experimenteller Beweis der Möglichkeit der Selbstentzündung des Heues (Grummetts) (Experimental Proof of the Possibility of Self-Ignition of Hay [hay variety])" *Annln. Chem. Justus Lebegs*, **167**, 361-368, 1873.
12. Medem, R., *Die Selbstentzündung von Heu, Steinkohlen und geolten Stoffen* (The Spontaneous Combustion of Hay, Coal and Oiled Materials), pIV, J. Abel, Greifswald, Germany, 1898. Partial translation by Dr. James Erb, unpublished, 1997.
13. Schwartz, E. von *Fire and Explosion Risks*, translated by T.C. Salter, Charles Griffin, London, 1904.
14. Brooks, C.K., and McCreary, A.R., *Are Steam Pipes Responsible for Fires?*, Bachelor's Thesis, Case Western Reserve University, 1908.

15. Bixel, E.C., and Moore, H.J., *Are Fires Caused by Steam Pipes?*, Bachelor's Thesis, Case Western Reserve University, 1910.
16. Bardsley, H. and Skeet, G., "The Effect of Preheating on the Ignition Temperature of Wood," *Fire Chemistry Note No. 30*, Department of Scientific and Industrial Research and Fire Offices' Committee Joint Fire Research Organization, London, 1950.
17. Bowes, P.C., *Self-heating: Evaluating and Controlling the Hazard*, p. 351 et seq., Her Majesty's Printing Office, London, 1984.
18. Palmer, K.N. and Tonkin, P.S., "The Ignition of Dust Layers on a Hot Surface," *Combustion and Flame*, **1**, 14-18, 1957.
19. Simms, D.L. and Roberts, V.E., "Effect of Prolonged Heating on the Subsequent Spontaneous Ignition of Oak," *J. of the Institute of Wood Science*, **5**, 29-37, 1960.
20. Hsieh, F.-Y. and Richards, G.N., "The Effect of Preheating of Wood on Ignition Temperature of Wood Char," *Combustion and Flame* **80**, 395-398, 1989.
21. Thomas, P.H., "An Approximate Theory of 'Hot Spot' Criticality," *Combustion and Flame*, **21**, 99-109, 1973.
22. Frank-Kamenetskii, D.A., *Diffusion and Heat Transfer in Chemical Kinetics*, 2nd ed., trans. J.P. Appleton, ch. 6, Plenum Press, New York, 1969.
23. Bowes, *op. cit.*, p. 35.
24. Beever, P.F., "Self-Heating and Spontaneous Combustion," In *The SFPE Handbook of Fire Protection Engineering*, 2nd ed., Ed. P.J. DiNenno, et al, pp 2-180 to 2-189, National Fire Protection Association, Quincy, MA, 1995.
25. Chen X. D. and Chong, L. V., "Some Characteristics of Transient Self-heating Inside an Exothermically Reactive Porous Solid Slab," *Process Safety and Environmental Protection: Trans. of the Inst. of Chemical Engineers, Part B*, **73**, 101-107, 1995.
26. Chong, L.V., Shaw, I.R., and Chen, X.D., "Thermal Ignition Kinetics of Wood Sawdust Measured by a Newly Devised Experimental Technique," *Process Safety Progress* **14**:4, 266-270, 1995.
27. Schaffer, E.L., "Smoldering Initiation in Cellulosics under Prolonged Low-Level Heating," *Fire Technology*, **16**:1, 22-28, 1980.
28. Wolters, F.C., Pagni, P.J., Frost, T.R., and Vanderhoof, D.W., "Size Constraints on Self-Ignition of Charcoal Briquets," *Fire Safety Journal*, In review, 1999.
29. Bowes, *op. cit.*, Eqn. 6.19.
30. Drysdale, D., *An Introduction to Fire Dynamics*, p. 219, John Wiley, New York, 1985.
31. Galligan, W.L., Gold, P.S., Ward, D.A., and Tinney, E.R., *Some Studies on the Combustion of Small Wooden Dowels*, Bulletin 294, Technical Extension Service, Washington State University, Pullman, WA, 1965.
32. Incropera, F.P and DeWitt, D.P., *Fundamentals of Heat and Mass Transfer*, 4th ed., p. 240, John Wiley, New York, 1996.
33. TenWolde, A., McNatt, J.D. and Krahn, L., *Thermal Properties of Wood and Wood Panel Products for Use in Buildings*, NTIS no. DOE/USDA-21697/1, Oak Ridge National Laboratory, Oak Ridge, TN, 1988.
34. Vyas, R.J., and Welker, J.R., "End Grain Ignition of Wood," *Journal of Fire and Flammability* **6**, 355-361, 1975.
35. Siau, J.F., *Flow in Wood*, p55, Syracuse University Press, Syracuse, NY, 1971.
36. High-Temp RTV Silicon, manufactured by Loctite Corp., Rocky Hill, CT.